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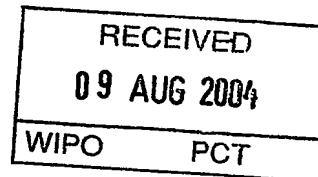
August 04, 2004

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APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A
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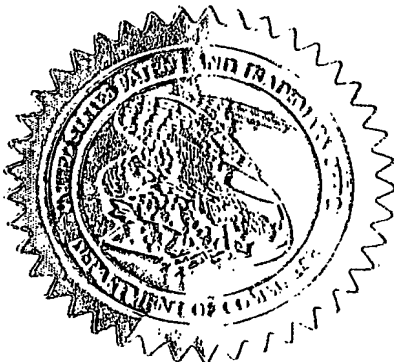
APPLICATION NUMBER: 60/473,870

FILING DATE: May 27, 2003

RELATED PCT APPLICATION NUMBER: PCT/US04/16431



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M. Tarver

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JC654 U.S. PTO

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PTO/SB/16 (10-01)

Approved for use through 10/31/2002. OMB 0651-0032

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53 (c).

Express Mail Label No. EU599925833US

11002 U.S. PTO

60/473870

05/27/03

| INVENTOR(S) | | | | | |
|--|------------------------|---|--|--|--|
| Given Name (first and middle [if any]) | Family Name or Surname | Residence (City and either State or Foreign Country) | | | |
| Zhen Yu | Yang | Wilmington, Delaware | | | |
| <input checked="" type="checkbox"/> Additional inventors are being named on the separately numbered sheets attached hereto | | | | | |
| TITLE OF THE INVENTION (500 characters max) | | | | | |
| Fuel Cell Membrane | | | | | |
| Direct all correspondence to: CORRESPONDENCE ADDRESS | | | | | |
| <input checked="" type="checkbox"/> Customer Number OR | | 23906 Type Customer Number Here | | *23906* PATENT TRADEMARK OFFICE | |
| <input type="checkbox"/> Firm or Individual Name | | | | | |
| Address | | | | | |
| Address | | | | | |
| City | | State | | ZIP | |
| Country | | Telephone | | Fax | |
| ENCLOSED APPLICATION PARTS (check all that apply) | | | | | |
| <input checked="" type="checkbox"/> Specification Number of Pages | | 24 | | <input type="checkbox"/> CD(s), Number | |
| <input checked="" type="checkbox"/> Drawing(s) Number of Sheets | | 1 | | <input type="checkbox"/> Other (specify) | |
| <input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76 | | | | | |
| METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT | | | | | |
| <input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. | | | | | |
| <input type="checkbox"/> A check or money order is enclosed to cover the filing fees | | | | | |
| <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: | | | | 04-1928 | |
| <input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached. | | | | 160 | |
| The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government. | | | | | |
| <input checked="" type="checkbox"/> No. | | | | | |
| <input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____ | | | | | |

Respectfully submitted,

Date

5/27/03

SIGNATURE

Daphne P. Fickes

TYPED or PRINTED NAME Daphne P. Fickes

TELEPHONE 302.999.6420

REGISTRATION NO.

36,509

(If appropriate)

Docket Number

CL2064 US PRV

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C., 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

60473870-222703

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FEE TRANSMITTAL
for FY 2003

Effective 01/01/2003. Patent fees are subject to annual revision.

☐ Applicant claims small entity status. See 37 CFR 1.27**TOTAL AMOUNT OF PAYMENT** (\$) **160.00****Complete if Known**

| | |
|----------------------|----------------|
| Application Number | To Be Assigned |
| Filing Date | May 27, 2003 |
| First Named Inventor | Zhen Yu Yang |
| Examiner Name | |
| Art Unit | |
| Attorney Docket No. | CL2064 US PRV |

METHOD OF PAYMENT (check all that apply)☐ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None☒ Deposit Account:Deposit
Account
Number
Deposit
Account
Name

04-1928

E. I. du Pont de Nemours and Company

The Director is authorized to: (check all that apply)

☒ Charge fee(s) indicated below ☒ Credit any overpayments☒ Charge any additional fee(s) during the pendency of this application☐ Charge fee(s) indicated below, except for the filing fee to the above-identified deposit account.**FEE CALCULATION****1. BASIC FILING FEE**

| Large Entity Fee Code (\$) | Small Entity Fee Code (\$) | Fee Description | Fee Paid |
|-------------------------------|-------------------------------|------------------------|---------------------------|
| 1001 750 | 2001 375 | Utility filing fee | |
| 1002 330 | 2002 165 | Design filing fee | |
| 1003 520 | 2003 260 | Plant filing fee | |
| 1004 750 | 2004 375 | Reissue filing fee | |
| 1005 160 | 2005 80 | Provisional filing fee | 160.00 |
| SUBTOTAL (1) | | | (\$) 160.00 |

2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

| Total Claims | Extra Claims | Fee from below | Fee Paid |
|--------------------|--------------|----------------|----------|
| Independent | -20** = | X 18 = | |
| Multiple Dependent | -3** = | X 84 = | |
| | | 280 = | |

| Large Entity Fee Code (\$) | Small Entity Fee Code (\$) | Fee Description |
|-------------------------------|-------------------------------|--|
| 1202 18 | 2202 9 | Claims in excess of 20 |
| 1201 84 | 2201 42 | Independent claims in excess of 3 |
| 1203 280 | 2203 140 | Multiple dependent claim, if not paid |
| 1204 84 | 2204 42 | ** Reissue independent claims over original patent |
| 1205 18 | 2205 9 | ** Reissue claims in excess of 20 and over original patent |

SUBTOTAL (2) (\$) **0.00**

**or number previously paid, if greater; For Reissues, see above

FEE CALCULATION (continued)**3. ADDITIONAL FEES**

Large Entity Small Entity

| Fee Code (\$) | Fee Code (\$) | Fee Description | Fee Paid |
|---------------|---------------|--|----------|
| 1051 130 | 2051 65 | Surcharge - late filing fee or oath | |
| 1052 50 | 2052 25 | Surcharge - late provisional filing fee or cover sheet | |
| 1053 130 | 1053 130 | Non-English specification | |
| 1812 2,520 | 1812 2,520 | For filing a request for ex parte reexamination | |
| 1804 920* | 1804 920* | Requesting publication of SIR prior to Examiner action | |
| 1805 1,840* | 1805 1,840* | Requesting publication of SIR after Examiner action | |
| 1251 110 | 2251 55 | Extension for reply within first month | |
| 1252 410 | 2252 205 | Extension for reply within second month | |
| 1253 930 | 2253 465 | Extension for reply within third month | |
| 1254 1,450 | 2254 725 | Extension for reply within fourth month | |
| 1255 1,970 | 2255 985 | Extension for reply within fifth month | |
| 1401 320 | 2401 160 | Notice of Appeal | |
| 1402 320 | 2402 160 | Filing a brief in support of an appeal | |
| 1403 280 | 2403 140 | Request for oral hearing | |
| 1451 1,510 | 1451 1,510 | Petition to institute a public use proceeding | |
| 1452 110 | 2452 55 | Petition to revive - unavoidable | |
| 1453 1,300 | 2453 650 | Petition to revive - unintentional | |
| 1501 1,300 | 2501 650 | Utility issue fee (or reissue) | |
| 1502 470 | 2502 235 | Design issue fee | |
| 1503 630 | 2503 315 | Plant issue fee | |
| 1460 130 | 1460 130 | Petitions to the Commissioner | |
| 1807 50 | 1807 50 | Processing fee under 37 CFR 1.17(q) | |
| 1806 180 | 1806 180 | Submission of Information Disclosure Stmt | |
| 8021 40 | 8021 40 | Recording each patent assignment per property (times number of properties) | |
| 1809 750 | 2809 375 | Filing a submission after final rejection (37 CFR 1.129(a)) | |
| 1810 750 | 2810 375 | For each additional invention to be examined (37 CFR 1.129(b)) | |
| 1801 750 | 2801 375 | Request for Continued Examination (RCE) | |
| 1802 900 | 1802 900 | Request for expedited examination of a design application | |

Other fee (specify)

*Reduced by Basic Filing Fee Paid

SUBTOTAL (3) (\$) **0.00****SUBMITTED BY**

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Date

5/27/03

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TITLE
FUEL CELL MEMBRANE
FIELD OF THE INVENTION

5 The present invention relates to a novel compound and its use in electrochemical cells as an electrolyte, and more particularly to the use of the compound in fuel cells.

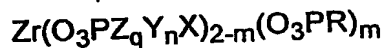
BACKGROUND OF THE INVENTION

10 Electrochemical cells, such as fuel cells and lithium-ion batteries are known. Depending on the operating conditions, each type of cell places a particular set of requirements upon the electrolytes used in them. For fuel cells, this is typically dictated by the type of fuel, such as hydrogen or methanol, used to power the cell and the composition of the membrane used to separate the electrodes. Proton-exchange membrane fuel cells; 15 powered by hydrogen as the fuel, could be run at higher operating temperatures than currently employed to take advantage of lower purity feed streams, improved electrode kinetics, better heat transfer from the fuel cell stack to improve its cooling. Waste heat is also employed in a useful fashion. However, if current fuel cells are to be operated at greater than 100 °C then they must be pressurized to maintain adequate hydration 20 of typical proton-exchange membranes, such as DuPont Nafion® perfluorosulfonic acid membrane, to support useful levels of proton conductivity.

25 There is an ongoing need to discover novel electrolytes that improve the performance of the latest generation of electrochemical cells, such as fuel cells and lithium-ion batteries, and form membrane materials that maintain adequate proton conductivity at lower levels of hydration.

SUMMARY OF THE INVENTION

30 In a first aspect, the invention provides a compound having the following structure:



wherein

35 X = a functional group such as CO₂H, PO(OH)₂, SO₃H, SO₂NHSO₂W, wherein W = aryl of 6 to 10 carbon atoms or Y;
Y = perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is 1-20 carbon atoms, or a fluorinated group containing at least

one substituent selected from the group consisting of oxygen, chlorine and bromine;

Z = alkylene of 1-12 carbon atoms, aryl of 6-10 carbon atoms, or a heterocyclic aryl group of 3-10 carbons atoms;

- 5 R = alkyl of 1-12 carbon atoms, aryl of 6-10 carbon atoms, substituted alkyl, or substituted aryl, wherein the substituent is selected from the group consisting of F, Cl, perfluoroalkyl, alkyl of 1-12 carbon atoms and aryl of 6-10 carbon atoms;

n = 0 or 1;

- 10 q = 0 or 1; and

m = 0 to 1.5; with the proviso that when n = 0, and q = 1, Z = at least one heterocyclic group having 3 to 10 carbon atoms, 1 to 5 nitrogen atoms and 0 to 4 oxygen atoms.

- 15 In a second aspect, the invention provides a functionalized phosphonic acid having the following structure:



wherein

- 20 X = a functional group such as CO_2H , $\text{PO}(\text{OH})_2$, SO_3H , $\text{SO}_2\text{NHSO}_2\text{W}$, wherein W = aryl of 6 to 10 carbon atoms or Y;

Y = perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is 1-20 carbon atoms, or a fluorinated group containing at least one substituent selected from the group consisting of oxygen, chlorine and

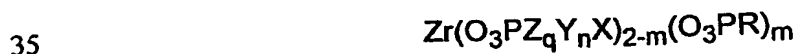
- 25 bromine;

Z = alkylene of 1-12 carbon atoms, aryl of 6-10 carbon atoms, or a heterocyclic aryl group of 3-10 carbons atoms;

n = 0 or 1; and

- 30 q = 0 or 1; with the proviso that when n = 0, and q = 1, Z = at least one heterocyclic group having 3 to 10 carbon atoms, 1 to 5 nitrogen atoms and 0 to 4 oxygen atoms.

In a third aspect, the invention provides a solid electrolyte membrane comprising a compound having the following structure:



wherein

X = a functional group such as CO_2H , $\text{PO}(\text{OH})_2$, SO_3H , $\text{SO}_2\text{NHSO}_2\text{W}$, wherein W = aryl of 6 to 10 carbon atoms or Y;

Y = perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is 1-20 carbon atoms, or a fluorinated group containing at least one substituent selected from the group consisting of oxygen, chlorine and bromine;

5 Z = alkylene of 1-12 carbon atoms, aryl of 6-10 carbon atoms, or a heterocyclic aryl group of 3-10 carbons atoms;

R = alkyl of 1-12 carbon atoms, aryl of 6-10 carbon atoms, substituted alkyl, or substituted aryl, wherein the substituent is selected from the group consisting of F, Cl, perfluoroalkyl, alkyl of 1-12 carbon atoms and aryl of
10 6-10 carbon atoms;

n = 0 or 1;

q = 0 or 1; and

m = 0 to 1.5; with the proviso that when n = 0, and q = 1, Z = at least one heterocyclic group having 3 to 10 carbon atoms, 1 to 5 nitrogen atoms and
15 0 to 4 oxygen atoms. These membranes are particularly useful at temperatures of at least 100 °C. Typically the compound is imbibed into a porous support to form the solid polymer electrolyte membrane.

In a fourth aspect, the invention provides a catalyst coated membrane comprising a solid electrolyte membrane having a first surface
20 and a second surface, an anode present on the first surface of the solid electrolyte membrane, and a cathode present on the second surface of the solid electrolyte membrane, wherein the solid electrolyte membrane comprises a compound having the following structure:



wherein

X = a functional group such as CO_2H , $\text{PO}(\text{OH})_2$, SO_3H , $\text{SO}_2\text{NHSO}_2\text{W}$, wherein W = aryl of 6 to 10 carbon atoms or Y;

30 Y = perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is 1-20 carbon atoms, or a fluorinated group containing at least one substituent selected from the group consisting of oxygen, chlorine and bromine;

Z = alkylene of 1-12 carbon atoms, aryl of 6-10 carbon atoms, or a
35 heterocyclic aryl group of 3-10 carbons atoms;

R = alkyl of 1-12 carbon atoms, aryl of 6-10 carbon atoms, substituted alkyl, or substituted aryl, wherein the substituent is selected from the group

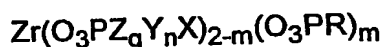
consisting of F, Cl, perfluoroalkyl, alkyl of 1-12 carbon atoms and aryl of 6-10 carbon atoms;

$n = 0$ or 1 ;

$q = 0$ or 1 ; and

- 5 $m = 0$ to 1.5 ; with the proviso that when $n = 0$, and $q = 1$, $Z =$ at least one heterocyclic group having 3 to 10 carbon atoms, 1 to 5 nitrogen atoms and 0 to 4 oxygen atoms. The compound may be introduced into the membrane by various methods, e.g. by imbibing into a porous support.

- 10 In a fifth aspect, the invention provides a fuel cell comprising a solid electrolyte membrane having a first surface and a second surface, wherein the solid electrolyte membrane comprises a compound having the following structure:



15

wherein

$X =$ a functional group such as CO_2H , $\text{PO}(\text{OH})_2$, SO_3H , $\text{SO}_2\text{NHSO}_2\text{W}$, wherein $W =$ aryl of 6 to 10 carbon atoms or Y ;

- 20 $Y =$ perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is 1-20 carbon atoms, or a fluorinated group containing at least one substituent selected from the group consisting of oxygen, chlorine and bromine;

$Z =$ alkylene of 1-12 carbon atoms, aryl of 6-10 carbon atoms, or a heterocyclic aryl group of 3-10 carbons atoms;

- 25 $R =$ alkyl of 1-12 carbon atoms, aryl of 6-10 carbon atoms, substituted alkyl, or substituted aryl, wherein the substituent is selected from the group consisting of F, Cl, perfluoroalkyl, alkyl of 1-12 carbon atoms and aryl of 6-10 carbon atoms;

$n = 0$ or 1 ;

- 30 $q = 0$ or 1 ; and

$m = 0$ to 1.5 ; with the proviso that when $n = 0$, and $q = 1$, $Z =$ at least one heterocyclic group having 3 to 10 carbon atoms, 1 to 5 nitrogen atoms and 0 to 4 oxygen atoms.

- 35 In the fifth aspect, the fuel cell further comprises an anode and a cathode present on the first and second surfaces of the electrolyte membrane. Gas diffusion backings may be present on the side of the anode or cathode away from the solid polymer electrolyte membrane. Alternately, gas diffusion electrodes comprising a gas diffusion backing

and an electrode may be present on the first and second surfaces of the solid polymer electrolyte membrane, wherein the electrode is adjacent the , solid polymer electrolyte membrane.

In the fifth aspect, the fuel cell further comprises a means for
5 delivering fuel to the anode, a means for delivering oxygen to the cathode, a means for connecting the anode and cathode to an external electrical load, methanol in the liquid or gaseous state in contact with the anode, and oxygen in contact with the cathode. The fuel is in the liquid or vapor phase. Some suitable fuels include hydrogen, and alcohols such as
10 methanol and ethanol, etc.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic illustration of a single cell assembly.

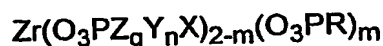
DETAILED DESCRIPTION OF THE INVENTION

The compounds of the invention that may be small molecules are
15 useful as electrolytes in the preparation of the solid electrolyte membranes. These solid electrolyte membranes may be used to make catalyst coated membranes that are a component of fuel cells.

Compound:

The compound of the invention has the following structure:

20



wherein

X = a functional group such as CO₂H, PO(OH)₂, SO₃H, SO₂NHSO₂W;

25 wherein W = aryl of 6 to 10 carbon atoms or Y;

Y = perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is 1-20 carbon atoms such as perfluoromethylene, perfluoroethylene, perfluoropropylene or a fluorinated group containing at least one substituent selected from the group consisting of oxygen,

30 chlorine and bromine such as CF₂CF₂OCF₂CF₂ or CF₂CFCF₃OCF₂CF₂;

Z = alkylene of 1-12 carbon atoms such as methylene, ethylene and propylene, aryl of 6-10 carbon atoms such as phenyl, or substituted phenyl, wherein the substituent is selected from the group consisting of, F, Cl, perfluoroalkyl such as trifluoromethyl, pentafluoroethyl, alkyl of 1-12

35 carbon atoms such as methyl, ethyl, propyl, butyl; naphthalene; or a heterocyclic aryl group of 3-10 carbons atoms such as benzimidazole, imidazole, pyrazole, triazole, thiazole, or oxadiazole;

R = alkyl of 1-12 carbon atoms such as methylene, ethylene and propylene; aryl of 6 - 12 carbon atoms such as benzene, or substituted benzene, naphthalene or substituted naphthalene; wherein the substituent is selected from the group consisting of F, Cl, perfluoroalkyl such as trifluoromethyl, pentafluoroethyl, alkyl of 1-12 carbon atoms such as methyl, ethyl, propyl, butyl, more typically methyl, and aryl of 6-12 carbon atoms such as benzene, or substituted benzene, wherein the substituent is selected from the group consisting of F, Cl, perfluoroalkyl such as trifluoromethyl, pentafluoroethyl, and alkyl of 1-12 carbon atoms such as methyl, ethyl, propyl, butyl;

n = 0 or 1;

q = 0 or 1;

m = 0 to 1.5; and with the proviso that when n = 0, and q = 1, Z =

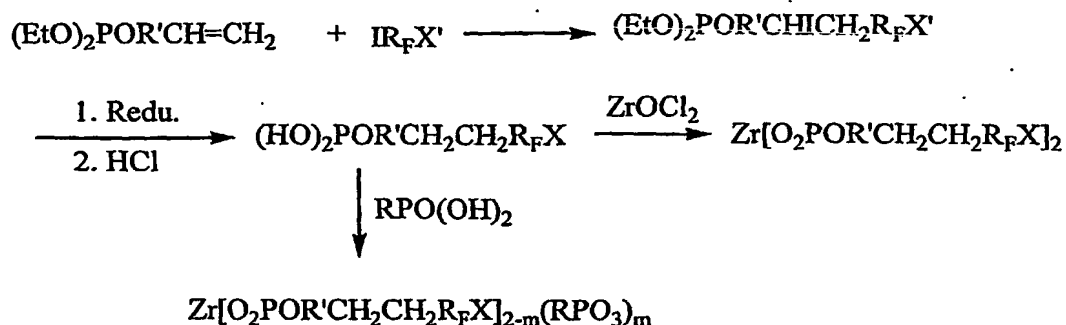
heterocyclic groups having 3 to 12 carbon atoms such as benzimidazole, imidazole, pyrazole, triazole, thiazole, or oxadiazole; more typically 3 to 8 carbon atoms, 1 to 5 nitrogen atoms, more typically 2 to 3 nitrogen atoms, and 0 to 4 oxygen atoms, more typically 0 to 2 oxygen atoms.

Some suitable heterocyclic groups include, benzimidazole, imidazole or oxadiazole. Some suitable compounds include $\text{Zr}(\text{HO}_2\text{CCF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PO}_3)_2$, $\text{Zr}(\text{H}_2\text{O}_3\text{PCF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PO}_3)_2$, $\text{Zr}(\text{HO}_3\text{SCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PO}_3)_2$, Zirconium (2-benzimidazolyl-2-ethylphosphonate), Zirconium (2-imidazolyl-2-ethylphosphonate), Zirconium (2-pyrazolyl-2-ethylphosphonate), Zirconium (2-oxadiazolyl-2-ethylphosphonate)

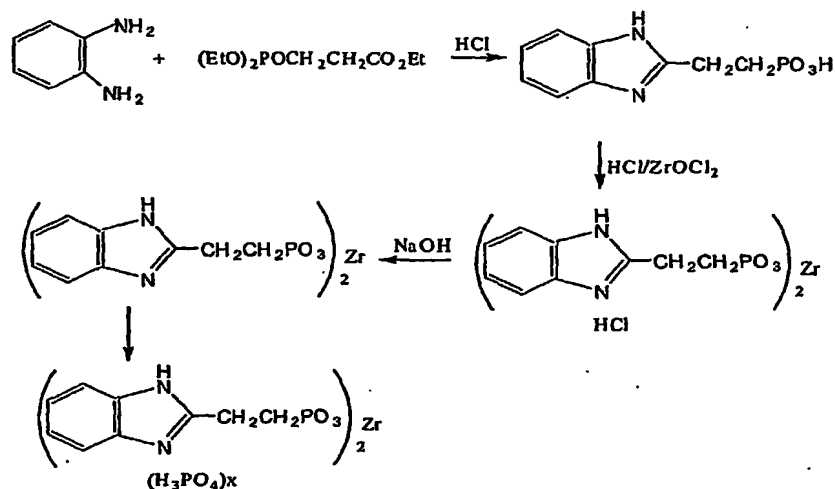
The compound may be prepared by several reaction steps from iodo substituted perfluoroalkylene functionalized compounds such as $\text{IR}_\text{F}\text{X}'$, where R_F is perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is 1-20 carbon atoms such as perfluoromethylene, perfluoroethylene or a fluorinated group containing substituents selected from the group consisting of oxygen, chlorine and bromine such as $\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2$, $\text{CF}_2\text{CFCF}_3\text{OCF}_2\text{CF}_2$, and X' is a precursor group such as SO_2F , $\text{PO}(\text{OEt})_2$ or CO_2Et of functionalized groups X, such as SO_3H , $\text{SO}_2\text{NSO}_2\text{CF}_3$, $\text{PO}(\text{OH})_2$, CO_2H . Addition of $\text{IR}_\text{F}\text{X}'$ to alkenylphosphonates such as diethyl allylphosphonate gives the corresponding adducts with a radical initiator such as benzoyl peroxide or metals such as Cu and $\text{Pd}(\text{PPh}_3)_4$ or salts such as $\text{Na}_2\text{S}_2\text{O}_4$. Adducts were reduced to remove iodine with a reducing reagent such as Bu_3SnH , Zn/HCl , Zn/NiCl_2 and so on. Finally, hydrolysis of the phosphonate with

aqueous acid such as aqueous HCl produced the corresponding phosphonic acid, which reacted with ZrOCl_2 in acidic water to give a compound $\text{Zr}[\text{O}_2\text{POR}'\text{CH}_2\text{CH}_2\text{R}_\text{F}\text{X}]_2$.

- 5 In the presence of other phosphonic acids, the mixed Zirconium phosphonate was formed as shown by this reaction:



- 10 Alternatively, functionalized phosphonic acid may be directly reacted with ZrOCl_2 in acidic water. This is particularly used for the production of Zr phosphonate containing heterocyclic ring structures such as benzimidazole, imidazole, pyrazole, triazole, thiazole, or oxadiazole; A typical example includes the following:



15 Membrane:

The compound identified above is useful in forming a solid electrolyte membrane, typically capable of operating at a temperature of at least 100 °C. In a first method, the electrolyte may be directly pressed into

thin films or a mixture of the electrolyte with other thermally and chemically stable polymers may be pressed into a film.

5 In a second method the electrolyte may be ground to a fine powder, and then dispersed in polymeric solution such as polyvinylidene fluoride in organic solvent. The dispersion may then be cast into a thin film on a glass plate and baked to remove solvent.

10 In a third method a mixture of the electrolyte and optionally a crosslinkable monomer may be poured into a porous support followed by drying, with or without heat, to insure that the electrolyte stayed in the porous structure.

The porous support of the membrane may be made from a wide range of components. Some examples include porous supports made from hydrocarbons such as a polyolefin, e.g., polyethylene, polypropylene, polybutylene, copolymers of those materials, and the like. Perhalogenated
15 polymers such as polychlorotrifluoroethylene may also be used. For resistance to thermal and chemical degradation, the support typically is made of a highly fluorinated polymer, most preferably perfluorinated polymer.

For example, the polymer for the porous support can be a
20 microporous film of polytetrafluoroethylene (PTFE) or a copolymer of tetrafluoroethylene with other perfluoroalkyl olefins or with perfluorovinyl ethers. Microporous PTFE films and sheeting are known which are suitable for use as a support layer. For example, U. S. Pat. No. 3,664,915 discloses uniaxially stretched film having at least 40% voids. U.S. Pat.
25 Nos. 3,953,566, 3,962,153 and 4,187,390 disclose porous PTFE films having at least 70% voids.

Alternatively, the porous support may be a fabric made from fibers of the support polymers discussed above woven using various weaves, such as the plain weave, basket weave, leno weave, or others. A
30 membrane suitable for the practice of the invention can be made by coating the porous support fabric with the compound, also known as the electrolyte, of the invention to form a composite membrane. To be effective the coating should typically be on both the outside surfaces as well as distributed through the internal pores of the support. This may be
35 accomplished by impregnating the porous support with a solution or dispersion of the solid electrolyte, using a solvent that is not harmful to the compound or the support, and under impregnation conditions that provide improved imbibing of the compound solution or dispersion into the support.

This results in a thin, even coating of the compound on the support. The support with the solution/dispersion is dried with or without heat to form the membrane. If desired, thin films of the solid electrolytes can be laminated to one or both sides of the impregnated porous support to prevent bulk
 5 flow through the membrane that can occur if large pores remain in the membrane after impregnation. It is preferred for the compound to be present as a continuous phase within the membrane.

In a fourth method the solid electrolyte may be imbibed in-situ into inorganic materials such as glass paper. The glass or other porous
 10 membranes first absorb aqueous ZrOCl_2 solution, and may then be immersed in a solution of $(\text{HO})_2\text{OPZ}_q\text{Y}_n\text{X}$ to form a supporting membrane containing the electrolyte.

Fuel Cell:

As shown in Figure 1, the fuel cell comprises a catalyst coated
 15 membrane (CCM) (10) in combination with at least one gas diffusion backing (GDB) (13) to form an unconsolidated membrane electrode assembly (MEA). The catalyst coated membrane (10) comprises an ion exchange polymer membrane (11) discussed above and catalyst layers or electrodes (12) formed from an electrocatalyst coating composition. The
 20 fuel cell is further provided with an inlet (14) for fuel, such as liquid or gaseous alcohols, e.g. methanol and ethanol, or hydrogen; an anode outlet (15); a cathode gas inlet (16); a cathode gas outlet (17); aluminum end blocks (18) tied together with tie rods (not shown); a gasket for sealing (19); an electrically insulating layer (20); graphite current collector blocks
 25 with flow fields for gas distribution (21); and gold plated current collectors (22).

The fuel cell utilizes a fuel source that may be in the liquid or gaseous phase, and may comprise hydrogen, or an alcohol. Typically a methanol/water solution is supplied to the anode compartment and air or
 30 oxygen supplied to the cathode compartment.

CATALYST COATED MEMBRANE (CCM):

A variety of techniques are known for CCM manufacture which apply an electrocatalyst coating composition similar to that described above onto the solid fluorinated polymer electrolyte membrane. Some
 35 known methods include spraying, painting, patch coating and screen, decal, pad or flexographic printing.

In one embodiment of the invention, the MEA (30), shown in Figure 1, may be prepared by thermally consolidating the gas diffusion

backing (GDB) with a CCM at a temperature of under 200°C, preferably 140-160°C. The CCM may be made of any type known in the art. In this embodiment, an MEA comprises a solid electrolyte (SPE) membrane with a thin catalyst- binder layer disposed thereon. The catalyst may be supported (typically on carbon) or unsupported. In one method of preparation, a catalyst film is prepared as a decal by spreading the catalyst ink on a flat release substrate such as Kapton® polyimide film (available from the DuPont Company). After the ink dries, the decal is transferred to the surface of the SPE membrane by the application of pressure and heat, followed by removal of the release substrate to form a catalyst coated membrane (CCM) with a catalyst layer having a controlled thickness and catalyst distribution. Alternatively, the catalyst layer is applied directly to the membrane, such as by printing, and then the catalyst film is dried at a temperature not greater than 200°C.

The CCM, thus formed, is then combined with a GDB to form the MEA (30). The MEA is formed, by layering the CCM and the GDB, followed by consolidating the entire structure in a single step by heating to a temperature no greater than 200°C, preferably in the range of 140-160°C, and applying pressure. Both sides of the MEA can be formed in the same manner and simultaneously. Also, the composition of the catalyst layer and GDB could be different on opposite sides of the membrane.

The invention is further illustrated by the following examples.

EXAMPLES

25 Method of Measuring Through-plane, High-temperature, No-water-added Membrane Conductivity:

The conductivity of the pellets or films was measured by a technique in which the current flows through (perpendicular to) the plane of the pellet or films. A lower electrode was formed from a 12.7 mm diameter stainless steel rod and an upper electrode was formed from a 6.35 mm diameter stainless steel rod. The rods were cut to length, their ends polished, and then they were gold plated. A stack was formed consisting of lower electrode / GDE / film / GDE / upper electrode. The GDE (gas diffusion electrode) was obtained from DeNora E-TEK, Somerset, NJ, and was a catalyzed ELAT® comprising carbon cloth, a microporous layer, Pt catalyst, and a 0.6-0.8 mg/cm² Nafion® application over the catalyst layer. The lower GDE was punched out as a 9.5 mm diameter disk, while the film and the upper GDE were punched out as

6.35 mm diameter disks to match the upper electrode. The stack was assembled and held in place in a block of machinable glass ceramic (Corning MACOR®) that had a 12.7 mm diameter hole drilled into the bottom of the block, that accepted the lower electrode. A concentric
 5 6.4 mm diameter hole was drilled into the top of the block, that accepted the upper electrode. A force of 270 N was applied to the stack by means of a clamp and calibrated spring. This produced a pressure of 8.6 MPa in the active area under the upper electrode, insuring low impedance ionic
 10 measurements at temperatures of 25 °C to 180 °C. The real part of the AC impedance of the fixture containing the sample film was measured at a frequency of 100 kHz (R_s) using a potentiostat/frequency response analyzer (PC4/750™ potentiostat with EIS software), (Gamry Instruments, Warminster, PA). The fixture short (R_f) was also determined by measuring
 15 the real part of the 100 kHz AC impedance of the fixture assembled with the stack and both GDE's, but without the film. The conductivity was calculated as

$$\kappa = t / ((R_s - R_f) \times 0.317 \text{ cm}^2),$$

20

where t was the thickness of the pellets or films in cm.

Method of Measuring In-plane Membrane Conductivity:

The membrane sample was loaded on a four point conductivity probe. The probe has a base plate that measures 1.9" x 1.5" x 0.385" and
 25 a cover plate 1.9" x 1.23" x 0.25". Four 0.5" long platinum wires (30 GA, Hauser and Miller Precious Metals) were fixed on top of four 0.05" wide ridges along the width direction of the base plate. The outer two probes has a spacing of 1" and the inner two probes has a spacing of 0.4". In
 30 between the ridges, the space was open so that the membrane was exposed to the environment. The membrane sample, typically 1 cm wide and 3.25 cm long was pressed against the four platinum probes with the cover plate by a clamp. The membrane was also exposed to the
 35 environment on the cover plate side, which also had the openings. The four platinum wires were connected electrically to a Solatron® impedance measurement system consisting of a SI1287 electrochemical interface and
 a 1255B frequency response analyzer. To measure the membrane conductivity, the probe was dipped into a 500 mL glass beaker filled with the desired solution so that the membrane was fully exposed to the

solution. The glass beaker was wrapped with heating tape, which was connected to a digital thermal controller. The thermocouple of the controller was immersed in the solution so that the solution temperature was precisely controlled.

- 5 Since the solution itself may have finite conductivity, it was important to correct for that in the measurement. This was accomplished by measuring separately the resistances of the cell when the membrane sample was loaded (R) and when a thin Teflon® film was loaded (R_0). The resistance (R_s) due to the sample was then calculated by the formula:
- 10 $R_s = R \times R_0 / (R_0 - R)$. The sample membrane conductivity was then calculated by the formula: $\sigma = L / (R_s \times A)$ where σ was conductivity (S/cm), L (cm) was the spacing between the inner two wires and A (cm²) was the cross sectional area of the membrane.

Example 1:

- 15 (EtO)₂POCH₂CH₂CH₂CF₂CO₂Et was prepared using the following procedure:

- A flask was charged with 4.0 g of NiCl₂/6H₂O, 13.0 g of Zn powder, 200 mL of THF and 3 mL of water. The resulting mixture was stirred at room temperature for 30 min 35.0 g of diethyl allylphosphonate and 50.0 g
- 20 of ICF₂CO₂Et were added, the mixture was stirred at room temperature overnight, and then poured into aqueous NH₄Cl solution. Solid was removed by filtration and the filtrate was extracted with ether (300 mL X 3). The combined ether layers were washed with water, dried over MgSO₄. After removal of the ether, the residue was distilled to give 19.4 g of the
- 25 title product, bp 113°C/5 mmHg. ¹H NMR: 4.25 (q, J = 7 Hz, 2H), 4.01 (m, 4H), 2.10 (m, 2H), 2.75 (m, 4H), 1.30 (m, 9H). ¹⁹F NMR: -105.6 (m). HRMS: Calcd. for C₁₁H₂₁O₅F₂P₁: 303.1173. Found: 303.1169.

(EtO)₂POCH₂CH₂CH₂CF₂CO₂Et was used to prepare (HO)₂POCH₂CH₂CH₂CF₂CO₂H using the following procedure:

- 30 A mixture of 19.0 g of (EtO)₂POCH₂CH₂CH₂CF₂CO₂Et and 50 mL of conc. HCl was refluxed for 7 days. After removal of all volatiles, the residue was dried under vacuum to give 11.8 g of the title compound.

- A glass tube was charged with the title compound and water in a ratio of 85 to 1 by weight. A liquid conductivity probe was inserted into the
- 35 tube and the unsealed tube was mounted in a controlled-temperature oven. The AC impedance was measured at 1 kHz as the tube was twice heated to 150 °C and cooled in 25 °C steps. The following conductivities were calculated using a cell constant for the probe measured using a NIST

traceable conductivity calibration standard for 0.1 siemens. The sample has conductivity of 129 mS/cm at 80°C and 4.69 mS/cm at 120°C.

(HO)₂POCH₂CH₂CH₂CF₂CO₂H was used to prepare Zr(O₃PCH₂CH₂CH₂CF₂CO₂H)₂ using the following procedure:

- 5 1.6 g (5 mmol) of ZrOCl₂/8H₂O was dissolved in 30 mL of water and 4.5 mL of 50% HF and then poured in to a solution of 2.18 g (10 mmol) of (HO)₂OPCH₂CH₂CH₂CF₂CO₂H in 20 mL of water. After being stirred at 70-80°C for 3 days and at room temperature for 16 hrs, the resulting mixture was transferred into a glass tube and centrifuged. Solids
10 were separated and washed with water thrice, and dried in a vacuum oven at 90°C to give 2.3 g of Zr(O₃PCH₂CH₂CH₂CF₂CO₂H)₂. The pellet (0.3 cm diameter in size) was pressed at room temperature and conductivity, measured using the procedure described above, was found to be 0.01 mS/cm at 150°C.

15 Example 2:

(HO)₂OPCH₂CH₂CH₂CF₂PO(OH)₂ was prepared using the following procedure:

- A mixture of 28.51 g of diethyl allylphosphonate, 47.1 g of ICF₂PO(OEt)₂, 0.98 g of Cu powder in 120 mL of CH₃CN was stirred at
20 80°C for 8 hours. After removal of volatiles, the residue was diluted with ether, filtered, evaporated to give 61.0 g of (EtO)₂OPCH₂CHICH₂CF₂PO(OEt)₂. HRMS: calcd. for C₁₁H₂₁O₅F₂P₁: 303.11729. Found: 303.11686.

- A flask was charged with 0.24 g of NiCl₂/6H₂O, 2.0 g of Zn powder,
25 100 mL of THF and 0.5 mL of water. The resulting mixture was stirred at room temperature for 20 min. 9.2 g of (EtO)₂OPCH₂CHICH₂CF₂PO(OEt)₂ were added and the mixture was stirred at room temperature overnight and then filtered. The filtrate was evaporated and the residue was diluted with ether, washed with aqueous NH₄Cl solution, water and dried over
30 MgSO₄. After removal, 3.95 g of the ether, (EtO)₂OPCH₂CH₂CH₂CF₂PO(OEt)₂, were obtained. A mixture of 3.95 g of (EtO)₂OPCH₂CH₂CH₂CF₂PO(OEt)₂ and 40 mL of conc. HCl was refluxed for 2 days, and then evaporated and dried to give 2.8 g of product. ¹⁹F NMR: -112.9 (dt, J = 102 Hz, J = 18.8 Hz). ¹H NMR: 2.1(m, 2H), 1.70 (m, 4H).
35

Zr[O₃PCH₂CH₂CH₂CF₂PO(OH)₂]₂ was prepared using the following procedure:

0.71 g (2.2 mmol) of $\text{ZrOCl}_2/6\text{H}_2\text{O}$ was dissolved in 8 mL of water and 1.0 mL of 50% HF and then poured into a solution of 1.1 g (4.3 mmol) of $(\text{HO})_2\text{OPCH}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{PO}(\text{OH})_2$ in 17 mL of water. After being stirred at 70-80°C for 20 hr, and at room temperature for 24 hr, the

5 resulting mixture was transferred into a glass tube and centrifuged. Solids were separated and washed with water thrice, and dried in a vacuum oven at 100°C to give 0.71 g of $\text{Zr}[\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{PO}(\text{OH})_2]_2$.

The pellet was pressed at room temperature and conductivity (through plane) at 125°C, measured using the procedure described above,

10 was found to be 27.98 mS/cm.

Example 3:

$(\text{EtO})_2\text{OPCH}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ was prepared using the following procedure:

A mixture of 110.6 g of diethyl allylphosphonate, 277.6 g of

15 $\text{ICF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ was heated to 80 to 85°C under N_2 . 0.5 g of benzoyl peroxide was added and the reaction mixture was stirred for 1.5 hr. Additional 0.5 g of benzoyl peroxide was added and the mixture was stirred for 2 hr and these steps were repeated four more times. GC indicated no starting materials. The mixture was evaporated to remove

20 excess diethyl allylphosphonate. 120 mL of Bu_3SnH were added and the mixture was stirred until no starting material remained. It was then diluted with ether, and treated with aqueous KF solution to remove Bu_3SnI , washed with water and dried over MgSO_4 . After removal of the ether, 159.3 g of product were obtained. ^{19}F NMR: +44.4 (s, 1F), -83.7 (m, 2F),

25 -88.9 (m, 2F), -113.2(s, 2F), -118.8 (m, 2F). HRMS: Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_6\text{F}_9\text{P}_1\text{S}_1$: 479.03398: Found: 479.03253.

$(\text{HO})_2\text{OPCH}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ was prepared using the following procedure:

A mixture of 46.9 g of

30 $(\text{EtO})_2\text{OPCH}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ and conc. 200 mL of concentrated HCl was heated at 110°C for 4 days and evaporated to remove volatile to give product. ^{19}F NMR: +44.7 (s, 1F), -83.3 (m, 2F), -87.7 (m, 2F), -112.9 (s, 2F), -118.3 (m, 2F).

$(\text{HO})_2\text{OPCH}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}$ was prepared using

35 the following procedure:

A mixture of 10.0 g of

$(\text{EtO})_2\text{OPCH}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ and 2.5 g of LiOH in 60 mL of MeOH was stirred overnight and then filtered and evaporated to give

solids, which were boiled with dry CH_3CN (3x60 mL), filtered and the filtrates were evaporated to give 10.1 g of product. ^{19}F NMR indicated no sulfonyl fluoride peak. The solids were refluxed with 80 mL of conc. HCl for 2 days. After removal of volatiles, 8.2 grams of residue were obtained.
 5 ^{19}F NMR: -82.9 (m, 2F), -88.5 (s, 2F), -118.0 (m, 2F), -118.5 (s, 2F). 7.2 g of solids was dissolved in water and run through an ion exchange column at two drops per minute and then evaporated and dried at 100°C in full vacuum to give 6.65 g of wax solids.

10 $\text{Zr}[\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}]_2$ was prepared using the following procedure:

0.39 g (1.2 mmol) of $\text{ZrOCl}_2/8\text{H}_2\text{O}$ was dissolved in 5 mL of water and then poured in to a solution of 1.0 g (2.38 mmol) of $(\text{HO})_2\text{OPCH}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}$ in 5 mL of water. After being stirred at $70\text{--}80^\circ\text{C}$ for 20 hours, the mixture was then heated in a
 15 vacuum oven at 85°C for 54 hrs and at 110°C for 6 hrs. 1.03 g of brown solid were obtained, that were ground into a fine powder, and pressed into pellets. Conductivity, measured using the procedure described above, was found to be 15.10 mS/cm at 150°C .

Example 4:

20 Benzimidazolyl-2-ethylenephosphonic acid was prepared using the following procedure:

A mixture of 10.8 g (0.1 mol) of 20.6 mL (0.093 mol), 41.7 g of concentration HCl and 41.7 g of water was refluxed 15 hr and then neutralized with 50% NaOH to pH = 14. The reaction mixture was
 25 extracted with CH_2Cl_2 (3x100 mL) and aqueous layer comprised of (sodium benzimidazolyl-2-ethylenephosphonate) was treated with concentrated HCl to pH = 5. Solids were filtered, washed with water for five times, dried in air and then in a vacuum oven at 60°C for 24 hr to give 15.6 g of product.

30 $\text{Zr}(\text{benzimidazolyl-2-ethylenephosphonate})$ was prepared using the following procedure:

A solution of 1.5 g of benzimidazolyl-2-ethylenephosphonic acid in 35 mL of water and 7 mL of con. HCl was poured into a solution of 0.806 g (2.5 mmol) of $\text{ZrOCl}_2/6\text{H}_2\text{O}$. The resulting mixture was stirred at 80°C for
 35 16 hrs and at room temperature for 48 hrs. After removal of the liquid, the solid was washed with aqueous NaOH to a pH = 8, and then washed with water and dried in a vacuum oven to give 1.5 g of powder. This was pressed to a pellet with thickness of 0.885 mm. Conductivity, measured

using a through-plane high temperature conductivity measurement technique described above, was 1.45 mS/cm at 100°C and 2.30 mS/cm at 125°C.

5 Zr(benzimidazolyl-2-ethylenephosphonate) in the presence of HF was prepared using the following procedure:

A solution of 4.5 g of benzimidazolyl-2-ethylenephosphonic acid in 50 mL of water and 12 mL of conc. HCl was poured into a solution of 3.22 g (10.0 mmol) of $\text{ZrOCl}_2/6\text{H}_2\text{O}$, 5.1 mL of 51% HF and 20 mL of water. The resulting mixture was stirred at 80°C for 18 hrs and at room
10 temperature for 24 hr, and then transferred into a glass tube and centrifuged. After removal of the top layer, the white solid was dried in a vacuum oven at 90°C for 24 hr and suspended in EtOH. The suspension was neutralized with 10% KOH solution to pH = 8.5. The solid was collected after centrifugation, washed with water and dried in the vacuum
15 oven at 90°C to give 1.93 g of white solid, that was pressed into a pellet with a thickness of 0.887 mm. Conductivity, measured using the procedure described above, was found to be 1.80 mS/cm at 100°C.

Example 5:

This example used a modified ceramic fiber sheet, product # ASPA-
20 1, from ZIRCAR ceramics, Inc., Florida, NY. The sheet nominally contained 51 wt % silica, 45 wt % alumina, and 4% hydrocarbon binder. The original binder was burned off in an 800°C furnace for 4 hours. The sheet was then saturated with a 2 % solution of Kynar® 741 PVDF resin (Atofina Chemicals, Inc., Philadelphia, PA) in dimethylacetamide, allowed
25 to sit for 5 minutes, and dried in a vacuum oven at 110°C for 1 hour. The sheet was immersed in a solution of 2.6 g of ZrOCl_2 and 25 mL of water at room temperature overnight. The film was transferred into a solution of 1.5 g of $(\text{HO})_2\text{POCH}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CO}_2\text{H}$ in 20 mL of water at 85°C for 8 hr and at held at room temperature for 2 days. The film was removed and
30 washed with de-ionized water 5 times and dried in a vacuum oven at 100°C overnight to give a membrane weighing 0.760 g (137% weight increase).

The membrane was loaded in an in-plane conductivity test cell containing a four-point probe as described above. The probe fixture
35 placed four parallel platinum wires in contact with the sample. Current was measured though the outer wires while the voltage response was measured across a 1 cm gap between the inner wires. The AC

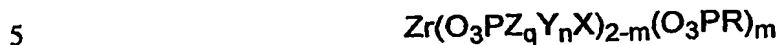
impedance was measured at 1 kHz, where the impedance is dominated ionic conductance. The film had conductivity 30 mS/cm at 80°C.

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CLAIMS

What is claimed is:

1. A compound having the following structure:



wherein

X = a functional group such as CO_2H , $\text{PO}(\text{OH})_2$, SO_3H , $\text{SO}_2\text{NHSO}_2\text{W}$, wherein W = aryl of 6 to 10 carbon atoms or Y;

10 Y = perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is 1-20 carbon atoms, or a fluorinated group containing at least one substituent selected from the group consisting of oxygen, chlorine and bromine;

Z = alkylene of 1-12 carbon atoms, aryl of 6-10 carbon atoms, 15 or a heterocyclic aryl group of 3-10 carbons atoms;

R = alkyl of 1-12 carbon atoms, aryl of 6-10 carbon atoms, substituted alkyl, or substituted aryl, wherein the substituent is selected from the group consisting of F, Cl, perfluoroalkyl, alkyl of 1-12 carbon atoms and aryl of 6-10 carbon atoms;

20 n = 0 or 1;

q = 0 or 1; and

m = 0 to 1.5; with the proviso that when n = 0, and q = 1, Z = at least one heterocyclic group having 3 to 10 carbon atoms, 1 to 5 nitrogen atoms and 0 to 4 oxygen atoms.

25 2. The compound of Claim 1 wherein Y = perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is selected from the group consisting of perfluoromethylene, perfluoroethylene and perfluoropropylene.

30 3. The compound of Claim 1 wherein Y is $\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2$ or $\text{CF}_2\text{CFCF}_3\text{OCF}_2\text{CF}_2$.

4. The compound of Claim 1 wherein Z = a heterocyclic aryl group comprising 3 to 8 carbon atoms, 1 to 5 nitrogen atoms, and 0 to 4 oxygen atoms.

35 5. The compound of Claim 4 wherein the heterocyclic aryl group comprises 3 to 8 carbon atoms, 2 to 3 nitrogen atoms, and 0 to 2 oxygen atoms.

6. The compound of Claim 4 wherein Z is selected from the group consisting of benzimidazole, imidazole, pyrazole, triazole, thiazole, and oxadiazole.

7. The compound of Claim 1 wherein R is selected from the group consisting of methyl, ethyl, propyl, butyl and phenyl.

8. The compound of Claim 1 selected from the group consisting of $\text{Zr}(\text{HO}_2\text{CCF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PO}_3)_2$, $\text{Zr}(\text{H}_2\text{O}_3\text{PCF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PO}_3)_2$, $\text{Zr}(\text{HO}_3\text{SCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PO}_3)_2$, Zirconium (2-benzimidazolyl-2-ethylphosphonate), Zirconium (2-imidazolyl-2-ethylphosphonate), Zirconium (2-pyrazolyl-2-ethylphosphonate), and Zirconium (2-oxadiazolyl-2-ethylphosphonate).

9. A functionalized phosphonic acid having the following structure:



wherein

X = a functional group such as CO_2H , $\text{PO}(\text{OH})_2$, SO_3H , $\text{SO}_2\text{NHSO}_2\text{W}$, wherein W = aryl of 6 to 10 carbon atoms or Y;

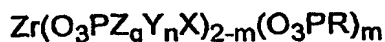
Y = perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is 1-20 carbon atoms, or a fluorinated group containing at least one substituent selected from the group consisting of oxygen, chlorine and bromine;

Z = alkylene of 1-12 carbon atoms, aryl of 6-10 carbon atoms, or a heterocyclic aryl group of 3-10 carbons atoms;

n = 0 or 1; and

q = 0 or 1; with the proviso that when n = 0, and q = 1, Z = at least one heterocyclic group having 3 to 10 carbon atoms, 1 to 5 nitrogen atoms and 0 to 4 oxygen atoms.

10. A solid electrolyte membrane comprising a compound having the following structure:



wherein

X = a functional group such as CO_2H , $\text{PO}(\text{OH})_2$, SO_3H , $\text{SO}_2\text{NHSO}_2\text{W}$, wherein W = aryl of 6 to 10 carbon atoms or Y;

Y = perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is 1-20 carbon atoms, or a fluorinated group containing at

least one substituent selected from the group consisting of oxygen, chlorine and bromine;

Z = alkylene of 1-12 carbon atoms, aryl of 6-10 carbon atoms, or a heterocyclic aryl group of 3-10 carbons atoms;

5 R = alkyl of 1-12 carbon atoms, aryl of 6-10 carbon atoms, substituted alkyl, or substituted aryl, wherein the substituent is selected from the group consisting of F, Cl, perfluoroalkyl, alkyl of 1-12 carbon atoms and aryl of 6-10 carbon atoms;

n = 0 or 1;

10 q = 0 or 1; and

m = 0 to 1.5; with the proviso that when n = 0, and q = 1, Z = at least one heterocyclic group having 3 to 10 carbon atoms, 1 to 5 nitrogen atoms and 0 to 4 oxygen atoms.

11. The solid electrolyte membrane of Claim 10 further comprising
15 a porous support.

12. The solid electrolyte membrane of Claim 10 wherein Y = perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is selected from the group consisting of perfluoromethylene, perfluoroethylene and perfluoropropylene.

20 13. The solid electrolyte membrane of Claim 10 wherein Y is $\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2$ or $\text{CF}_2\text{CFCF}_3\text{OCF}_2\text{CF}_2$.

14. The solid electrolyte membrane of Claim 10 wherein Z = a heterocyclic aryl group comprising 3 to 8 carbon atoms, 1 to 5 nitrogen atoms, and 0 to 4 oxygen atoms.

25 15. The solid electrolyte membrane of Claim 14 wherein the heterocyclic aryl group comprises 3 to 8 carbon atoms, 2 to 3 nitrogen atoms, and 0 to 2 oxygen atoms.

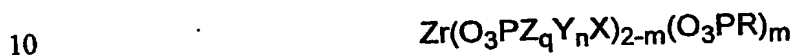
16. The solid electrolyte membrane of Claim 14 wherein Z is selected from the group consisting of benzimidazole, imidazole, pyrazole, triazole, thiazole, and oxadiazole.
30

17. The solid electrolyte membrane of Claim 10 wherein R is selected from the group consisting of methyl, ethyl, propyl, butyl and phenyl.

18. The solid electrolyte membrane of Claim 10 wherein the
35 compound is selected from the group consisting of $\text{Zr}(\text{HO}_2\text{CCF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PO}_3)_2$, $\text{Zr}(\text{H}_2\text{O}_3\text{PCF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PO}_3)_2$, $\text{Zr}(\text{HO}_3\text{SCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PO}_3)_2$, Zirconium (2-benzimidazolyl-2-ethylphosphonate), Zirconium (2-imidazolyl-2-

ethylphosphonate), Zirconium (2-pyrazolyl-2-ethylphosphonate), and Zirconium (2-oxadiazolyl-2-ethylphosphonate).

19. A catalyst coated membrane comprising a solid electrolyte membrane having a first surface and a second surface, an anode present on the first surface of the solid electrolyte membrane, and a cathode present on the second surface of the solid electrolyte membrane, wherein the solid electrolyte membrane comprises a compound having the following structure:



wherein

X = a functional group such as CO_2H , $\text{PO}(\text{OH})_2$, SO_3H , $\text{SO}_2\text{NHSO}_2\text{W}$, wherein W = aryl of 6 to 10 carbon atoms or Y;

- 15 Y = perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is 1-20 carbon atoms, or a fluorinated group containing at least one substituent selected from the group consisting of oxygen, chlorine and bromine;

- 20 Z = alkylene of 1-12 carbon atoms, aryl of 6-10 carbon atoms, or a heterocyclic aryl group of 3-10 carbon atoms;

R = alkyl of 1-12 carbon atoms, aryl of 6-10 carbon atoms, substituted alkyl, or substituted aryl, wherein the substituent is selected from the group consisting of F, Cl, perfluoroalkyl, alkyl of 1-12 carbon atoms and aryl of 6-10 carbon atoms;

- 25 n = 0 or 1;

q = 0 or 1; and

m = 0 to 1.5; with the proviso that when n = 0, and q = 1, Z = at least one heterocyclic group having 3 to 10 carbon atoms, 1 to 5 nitrogen atoms and 0 to 4 oxygen atoms.

- 30 20. The catalyst coated membrane of Claim 19 wherein the solid electrolyte membrane further comprising a porous support.

21. The catalyst coated membrane of Claim 19 wherein Y = perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is selected from the group consisting of perfluoromethylene, perfluoroethylene and perfluoropropylene.

- 35 22. The catalyst coated membrane of Claim 19 wherein Y is $\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2$ or $\text{CF}_2\text{CFCF}_3\text{OCF}_2\text{CF}_2$.

23. The catalyst coated membrane of Claim 19 wherein Z = a heterocyclic aryl group comprising 3 to 8 carbon atoms, 1 to 5 nitrogen atoms, and 0 to 4 oxygen atoms.

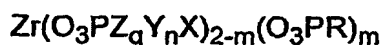
24. The catalyst coated membrane of Claim 23 wherein the heterocyclic aryl group comprises 3 to 8 carbon atoms, 2 to 3 nitrogen atoms, and 0 to 2 oxygen atoms.

25. The catalyst coated membrane of Claim 23 wherein Z is selected from the group consisting of benzimidazole, imidazole, pyrazole, triazole, thiazole, and oxadiazole.

26. The catalyst coated membrane of Claim 19 wherein R is selected from the group consisting of methyl, ethyl, propyl, butyl and phenyl.

27. The catalyst coated membrane of Claim 19 wherein the compound is selected from the group consisting of $\text{Zr}(\text{HO}_2\text{CCF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PO}_3)_2$, $\text{Zr}(\text{H}_2\text{O}_3\text{PCF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PO}_3)_2$, $\text{Zr}(\text{HO}_3\text{SCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PO}_3)_2$, Zirconium (2-benzimidazolyl-2-ethylphosphonate), Zirconium (2-imidazolyl-2-ethylphosphonate), Zirconium (2-pyrazolyl-2-ethylphosphonate), and Zirconium (2-oxadiazolyl-2-ethylphosphonate).

28. A fuel cell comprising a solid electrolyte membrane having a first surface and a second surface, wherein the solid electrolyte membrane comprises a compound having the following structure:



wherein

X = a functional group such as CO_2H , $\text{PO}(\text{OH})_2$, SO_3H , $\text{SO}_2\text{NHSO}_2\text{W}$, wherein W = aryl of 6 to 10 carbon atoms or Y;

Y = perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is 1-20 carbon atoms, or a fluorinated group containing at least one substituent selected from the group consisting of oxygen, chlorine and bromine;

Z = alkylene of 1-12 carbon atoms, aryl of 6-10 carbon atoms, or a heterocyclic aryl group of 3-10 carbons atoms;

R = alkyl of 1-12 carbon atoms, aryl of 6-10 carbon atoms, substituted alkyl, or substituted aryl, wherein the substituent is selected from the group consisting of F, Cl, perfluoroalkyl, alkyl of 1-12 carbon atoms and aryl of 6-10 carbon atoms;

$n = 0$ or 1 ;

$q = 0$ or 1 ; and

$m = 0$ to 1.5 ; with the proviso that when $n = 0$, and $q = 1$, $Z =$ at least one heterocyclic group having 3 to 10 carbon atoms, 1 to 5 nitrogen atoms and 0 to 4 oxygen atoms.

29. The fuel cell of Claim 28 further comprising an anode and a cathode present on the first and second surfaces of the solid electrolyte membrane.

30. The fuel cell of Claim 29 further comprising gas diffusion backings adjacent the anode and cathode.

31. The fuel cell of Claim 28 further comprising gas diffusion electrodes comprising a gas diffusion backing and an electrode present on the first and second surfaces of the solid polymer electrolyte membrane, wherein the electrode is adjacent the solid polymer electrolyte membrane.

32. The fuel cell of Claim 29 further comprising a means for delivering fuel to the anode, a means for delivering oxygen to the cathode, a means for connecting the anode and cathode to an external electrical load, methanol in the liquid or gaseous state in contact with the anode, and oxygen in contact with the cathode.

33. The fuel cell of Claim 28 wherein the fuel is hydrogen.

34. The fuel cell of Claim 28 wherein the fuel is an alcohol.

35. The fuel cell of Claim 34 wherein the fuel is methanol.

TITLE

FUEL CELL MEMBRANE

ABSTRACT OF THE DISCLOSURE

5 The present invention provides for a compound having the following structure: $Zr(O_3PZ_qY_nX)_{2-m}(O_3PR)_m$, wherein X = a functional group such as CO_2H , $PO(OH)_2$, SO_3H , SO_2NHSO_2W , wherein W = aryl of 6 to 10 carbon atoms or Y; Y = perfluoro-linear, branched or cyclic alkylene group, wherein the alkylene is 1-20 carbon atoms; or a fluorinated group containing at least one substituent selected from the group consisting of oxygen, chlorine and bromine; Z = alkylene of 1-12 carbon atoms, aryl of 6-10 carbon atoms, or a heterocyclic aryl group of 3-10 carbons atoms; R = alkyl of 1-12 carbon atoms, aryl of 6-10 carbon atoms, substituted alkyl, or substituted aryl, wherein the substituent is selected from the group consisting of F, Cl, perfluoroalkyl, alkyl of 1-12 carbon atoms and aryl of 6-10 carbon atoms; n = 0 or 1; q = 0 or 1; and m = 0 to 1.5; with the proviso that when n = 0, and q = 1, Z = at least one heterocyclic group having 3 to 10 carbon atoms, 1 to 5 nitrogen atoms and 0 to 4 oxygen atoms. The invention also provides a polymer electrolyte membrane, a catalyst coated membrane and a fuel cell having this compound.

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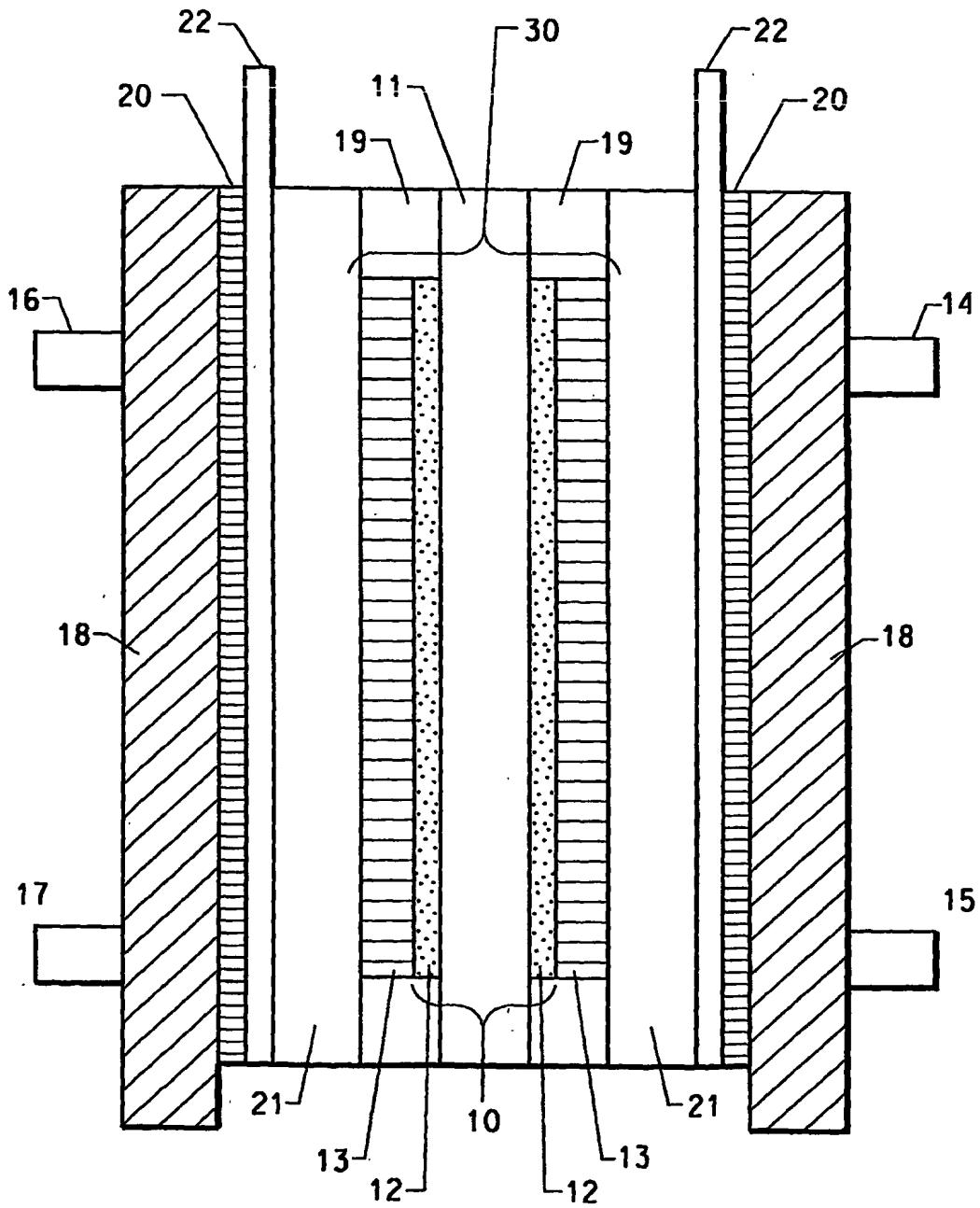


FIG. 1